PTO/SB/05 (09-04)
Approved for use through 07/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office. U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	S-0806-A
First Inventor	Greg A. Cunningham
Title	System And Methods For Dispensing
Express Mail Label No.	ER879782201US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: **Commissioner for Patents P.O. Box 1450 Alexandria VA 22313-1450**

1. ☑ **Fee Transmittal Form** (e.g., PTO/SB/17) *(Submit an original and a duplicate for fee processing)*
2. ☑ **Applicant claims small entity status.** See 37 CFR 1.27.
3. ☑ **Specification** *[Total Pages* 16 *]* Both the claims and abstract must start on a new page *(For information on the preferred arrangement, see MPEP 608.01(a))*
4. ☑ **Drawing(s)** *(35 U.S.C. 113)* *[Total Sheets* 7 *]*
5. **Oath or Declaration** *[Total Sheets* 2 *]*
   a. ☑ Newly executed (original or copy)
   b. ☐ A copy from a prior application (37 CFR 1.63(d)) *(for continuation/divisional with Box 18 completed)*
      i. ☐ DELETION OF INVENTOR(S) Signed statement attached deleting inventor(s) name in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).
6. ☐ **Application Data Sheet.** See 37 CFR 1.76
7. ☐ **CD-ROM or CD-R** in duplicate, large table or Computer Program *(Appendix)*
   ☐ Landscape Table on CD
8. **Nucleotide and/or Amino Acid Sequence Submission** *(if applicable, items a. – c. are required)*
   a. ☐ Computer Readable Form (CRF)
   b. Specification Sequence Listing on:
      i. ☐ CD-ROM or CD-R (2 copies); or
      ii. ☐ Paper
   c. ☐ Statements verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

9. ☐ **Assignment Papers** (cover sheet & document(s))
   Name of Assignee ______________________
10. ☐ **37 CFR 3.73(b) Statement** *(when there is an assignee)* ☑ **Power of Attorney**
11. ☐ **English Translation Document** *(if applicable)*
12. ☑ **Information Disclosure Statement** (PTO/SB/08 or PTO-1449)
    ☑ Copies of citations attached
13. ☐ **Preliminary Amendment**
14. ☑ **Return Receipt Postcard** (MPEP 503) *(Should be specifically itemized)*
15. ☐ **Certified Copy of Priority Document(s)** *(if foreign priority is claimed)*
16. ☐ **Nonpublication Request** under 35 U.S.C. 122(b)(2)(B)(i). Applicant must attach form PTO/SB/35 or equivalent.
17. ☐ Other: ______________________

18. If a CONTINUING APPLICATION, *check appropriate box, and supply the requisite information below and in the first sentence of the specification following the title, or in an Application Data Sheet under 37 CFR 1.76:*

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.: ....

Prior application information: *Examiner* ______________________ *Art Unit:* ______________________

19. CORRESPONDENCE ADDRESS

☑ The address associated with Customer Number: 2071 **OR** ☐ Correspondence address below

Name					
Address					
City		State		Zip Code	
Country		Telephone		Fax	

Signature		Date	January 31, 2005
Name (Print/Type)	Brenda C. Harvey	Registration No. (Attorney/Agent)	50,405

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : E21B 43/00

A1

(11) International Publication Number: WO 88/ 01010

(43) International Publication Date: 11 February 1988 (11.02.88)

(21) International Application Number: PCT/US87/01796

(22) International Filing Date: 24 July 1987 (24.07.87)

(31) Priority Application Numbers: 892,155
938,866

(32) Priority Dates: 30 July 1986 (30.07.86)
8 December 1986 (08.12.86)

(33) Priority Country: US

(71) Applicant: GREAT LAKES CHEMICAL CORPORATION [US/US]; P.O. Box 2200, Highway 52, N.W., West Lafayette, IN 47906 (US).

(72) Inventors: DADGAR, Ahmad ; 1018 Westridge Circle, Lafayette, IN 47905 (US). SHIN, Charles, C. ; 1909 Tanglewood Drive, Lafayette, IN 47905 (US).

(74) Agents: VITTUM, Daniel, W. Jr. et al.; Kirkland & Ellis, 200 E. Randolph Dr., Suite 6100, Chicago, IL 60601 (US).

(81) Designated States: GB (European patent), IT (European patent), NO.

Published
With international search report.
With amended claims.

(54) Title: CALCIUM-FREE CLEAR HIGH DENSITY FLUIDS

(57) Abstract

Clear, high density calcium-free fluids for use as completion, packing and perforation media in oil and gas well formations having high carbonate and/or high sulfate ion concentrations are formulated from aqueous solutions of zinc bromide and one or more alkali metal bromides and have densities lying in the range of about 11.5 to 20.5 lb./gal and a pH lying in the range of about 1.0 to 7.5.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

CALCIUM-FREE CLEAR HIGH DENSITY FLUIDS

CROSS-REFERENCE

This application is a continuation-in-part of applicants' copending application, Serial No. 892,155, filed July 30, 1986.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to the preparation and use of solids-free fluids for oil and gas drilling, completion and workover operations. More particularly, the invention relates to new calcium-free fluids which may be used as completion, packer and perforating media in oil and gas drilling and completion operations when formations have high carbonate and/or high sulfate ion concentrations.

Description of the Prior Art

Special fluids known as drilling fluids are used in the drilling, completion, and workover of oil and gas wells. These fluids ideally perform the following functions: transport drill cuttings or solids debris to the surface; suspend cuttings and solids in lost circulation zones; counteract formation pressure; maintain borehole stability; cool and lubricate downhole equipment; aid the suspension of tool string and casing; minimize corrosion; and minimize damage to formation permeability.

Use of these drilling fluids has greatly increased the efficiency of operations at the well. However, problems with certain applications of these fluids have been encountered. For

example, when used in completion operations, these fluids leave a deposit of acid-insoluble filter cake in the bore hole which blocks production and is difficult to remove. Further, use of these fluids may permit entry of fresh water mud filtrates which can promote the hydration of naturally occurring clay materials which swell in volume and restrict permeability. Finally, because of the high alkalinity of many of these fluids, precipitation of insoluble hydroxides occurs along the filtration path, impeding production. These problems have been partially overcome by underreaming or acidizing of the bore hole if the damage is not severe.

In recent years, however, specialized solids free completion and workover fluids have been developed to help prevent this type of damage to formation permeability. These solids-free fluids are placed across the production zone during completion and workover operations performing the same functions as drilling fluids but minimizing formation damage. These solids-free completion fluids comprise concentrated salt-water solutions in the density range of about 10 to 21 pounds per gallon ("lb/gal" or "ppg") and may be used as perforation, gravel pack, packer, and workover media. Examples of these solutions include aqueous solutions of alkali and alkaline earth metal and zinc halides such as sodium chloride, sodium bromide, calcium chloride, calcium bromide, zinc bromide or mixtures thereof.

As disclosed in 1964 in U.S. Patent No. 3,126,950 ("'950"), concentrated solutions of zinc chloride and/or calcium chloride can be prepared and used as well completion fluids up to a density of about 17 lb/gal. As noted in the '950 patent, however, zinc chloride/calcium chloride solutions with densities greater than 14 lb/gal. have high ferrous metal corrosion rates and therefore cannot practically be used with most well and surface equipment. Further, solutions with densities in the

14 lb/gal. range are not highly effective for deep well drilling. As a result of these limitations, these completion fluids did not receive strong acceptance in the oil and gas industry.

Other solids-free completion fluids have been better received. These fluids comprise calcium bromide, calcium chloride, and water and have densities up to 15.1 lb/gal. See Plonka, "New Bromide Packer Fluids Cut Corrosive Problems," World Oil, April 1972, and Paul and Plonka "Solids-Free Completion Fluids Maintain Formation Permeability," SPE 4655, Las Vegas, September 30 - October 3, 1973. Unlike the fluids in the '950 patent, calcium bromide/calcium chloride fluids have very low corrosion rates, which can be further reduced with the addition of suitable corrosion inhibitors. Density limitations (15.1 lb/gal limit) and high crystallization point temperatures (68°F) of the calcium bromide/calcium chloride fluids, however, have made these fluids less than ideal for use in completion operations. Therefore demands for other new solids-free completion fluids have continued.

Another new system of completion fluids in the density range of 15.0 to 19.2 lb/gal was disclosed in 1981 in U.S. Patent No. 4,292,183, ("'183"). The '183 patent teaches mixtures of zinc bromide, calcium bromide, calcium chloride, and water which contain corrosion inhibitors capable of reducing the corrosion rate of mild steel coupons to less than 10 mpy at 250°F.

Although the introduction of these various new completion fluids have helped resolve many of the difficulties encountered in completion and workover operations, problems still remain. For example, use of completion fluids with significant zinc and calcium ion concentrations in subterranean wells containing carbonate or carbon dioxide result in precipitation of calcium and zinc carbonates. Further, it has been reported by

Shaughnessy, et al. in "Workover Fluids for Prudhoe Bay," February-July 1977 that the mixing of calcium chloride workover fluids with formation brines under certain conditions (i.e., at a pressure of 5000 psi and a temperature of 220° F) can lead to the precipitation of calcium carbonate within reservoir rock and, therefore, to formation damage. These problems have been partially resolved by utilizing sodium bromide completion and workover fluids in place of calcium ion containing solutions. However, sodium bromide solutions can only be used in shallow wells where high formation pressures are not encountered. Further, more recently, carbon dioxide or carbonate containing wells have been discovered which require drilling and completion fluids with fluid densities of at least 14-20 lb/gal, density ranges which are well above those of sodium bromide.

It is thus a primary object of the present invention to develop high density completion fluids that may be successfully used in sulfate and/or carbonate-containing wells, in the density range of 11.5 to 20.5 lb/gal.

It is a further object of the invention to develop high density completion fluids having pH values in the range of 1.0 to 7.5 for use in sulfate and/or carbonate containing wells.

An additional object of the invention is to develop high density calcium-free completion fluids for use in carbonate and/or sulfate containing wells which are economical.

Another object of the present invention is to develop high/density calcium-free completion fluids which may also contain corrosion inhibitors and viscosifying agents for downhole applications.

Further objects and uses of the present invention will also be obvious from the following disclosure.

SUMMARY OF THE INVENTION

The foregoing objects, advantages and features of this invention may be achieved with high-density calcium-free fluids adapted for use as completion, packing, and perforation media in well formations having high carbonate and/or sulfate concentrations comprising aqueous solutions of zinc bromide and one or more alkali metal bromide having densities in the range of about 11.5 to about 20.5 lb/gal and pH values in the range of about 1.0 to 7.5. Suitable alkali metal bromides include bromides of lithium, sodium and potassium as well as mixtures thereof. These solutions may also contain corrosion inhibitors to provide a non-corrosive environment for downhole applications, and viscosifiers for more effective use.

In its method aspect, the present invention involves injecting a high density calcium-free fluid into wells having a high carbonate and/or sulfate ion concentration.

The novelty of the fluids of this invention is that, contrary to the expectations of those skilled in the art, solutions obtained by substituting one or more alkali metal bromides for calcium bromide in zinc bromide/calcium bromide fluids may be used without precipitation of zinc salts when applied to carbonate and/or sulfate containing formation brines.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Calcium-free solutions for use as completions fluids in oil and gas formations containing high carbonate and/or sulfate

ion concentrations have been prepared. These solutions comprise mixtures of zinc bromide and one or more alkali metal bromide and water and have densities in the range of 11.5 to 20.5 lb/gal, preferably about 11.5-19.2 lb/gal, and pH values of about 1.0 to 7.5, preferably about 2.5 to 5.5.

Suitable alkali metal bromides which may be used in accordance with this invention include sodium bromide, potassium bromide, and lithium bromide. Mixtures of alkali metal bromides, especially mixtures of sodium and potassium bromides, may also be employed.

The relative concentrations or amounts of the different salt constituents used in these completion fluids are not critical and may be determined by convenience so long as the density and pH limitations are maintained. Desirably the compositions of zinc bromide and alkali metal bromides (LiBr, KBr, or NaBr) in these calcium-free fluids are about 1.0 - 77.0 wt.% and 1.0 - 54.0 wt.%, respectively. Preferably these compositions are 2-56% zinc bromide and 14-54% alkali metal bromide(s) by weight of the overall compositions.

In the case of the zinc bromide/sodium bromide fluids, the densities lie in the range of about 12.5 to 19.2 lb/gal. Density of zinc bromide/potassium bromide fluids lie in the range of about 11.5 to 19.2 lb/gal. Zinc bromide/lithium bromide fluids have densities lying in the range of about 13.5 to 18.0 lb/gal., and fluids composed of zinc bromide/sodium bromide/potassium bromide have densities of about 13.0 to 18.0 lb/gal.

The calcium free solutions of the present invention may be prepared by mixing a zinc bromide/alkali metal bromide base fluid with one or more monovalent alkali metal bromide solutions.

The zinc bromide/alkali metal bromide base fluids may be prepared by combining solid zinc bromide and water with a solid alkali metal bromide or an aqueous solution thereof. The zinc bromide/alkali metal bromide base fluids may also be prepared by dissolving dry alkali metal bromides(s) in aqueous zinc bromide solutions. For example, a 17.5 lb/gal. $ZnBr_2$/NaBr base fluid is prepared by adding 14.8g water to 60.8g 77 wt% $ZnBr_2$ solution, and then dissolving 24.4g 97% NaBr in the resulting solution to prepare 100g fluid. Different $ZnBr_2$/NaBr blends in the density range of 13.0-17.5 lb/gal. may be prepared by mixing appropriate volumes of 17.5 lb/gal. $ZnBr_2$/NaBr base fluid with 12.5 lb/gal. NaBr (46.0 wt.% NaBr in water).

Corrosion inhibitors such as thioglycolates and thiocyanates which effectively control corrosion rates of mild steel may also be added to the completion fluids of the present invention to control corrosion of downhole equipment. The reason for the use of corrosion inhibitors is that completion fluids which contain zinc bromide are more corrosive than fluids formulated with alkali and alkaline earth metal bromides (ie., LiBr, NaBr, KBr and $CaBr_2$). Therefore corrosion inhibitors are generally used when zinc bromide is present. British patent, GB 2 027 687, and German patent, Ger. offen. DE 3 316 677 A1l, disclose the use of various corrosion inhibitors, such as thioglycolates and thiocynates, in zinc containing fluids. Suitable corrosion inhibitors which are capable of assisting in the control of corrosion with the calcium-free fluids of this invention include alkali metal and ammonium thiocyanates and thioglycolates, calcium thioglycolate and mixtures thereof. In addition, especially preferred corrosion inhibitors for use in the solutions of this invention, most especially those containing 50 wt.% $ZnBr_2$ or more, are disclosed in copending United States patent application Serial No. 913,409, filed September 30, 1986. The corrosion inhibitors in accordance with the Serial No.

913,409 application include calcium thiocyanate and a mixture of sodium thiocyanate, ammonium thioglycolate, and sodium isoascorbate.

Viscosifiers may also be added to the completion fluids of the present invention to help increase these fluids' ability to suspend and remove cuttings from the well and to prevent significant loss of fluids to the formation. Natural polymers such as guar gum, xanthan gum, and hydroxyethyl cellulose ("HEC") may be used as viscosifier additives in drilling and completion fluids. Only HEC has been used extensively as a viscosifier for drilling and completion fluids in the density range of 10 to 19.2 lb/gal. HEC polymer, solvated with ethylene glycol or suspended in mineral oil, has been used to viscosify aqueous NaBr, $CaCl_2$, $CaBr_2$, and $ZnBr_2$ brines in the density range of 10.0 to 15.0 and from 16.5 to 19.2 lb/gal. This viscosifier however fails to viscosify zinc ion-containing fluids in the density range of 15.0 to 16.5 lb/gal. This failure is believed to be due to the structural changes of solvent and solute caused by the different concentration ratio of halogen to zinc ion. An especially preferred viscosifier system is disclosed in United States Patent application Serial No. 913,415, filed September 29, 1986.

The following Examples are provided for the purpose of further illustration of the preferred embodiment of the present invention and are not intended to be limitations on the disclosed invention.

EXAMPLE I.

Tables 1 through 6, present the weight percents ("wt %") of the various salt constituents used in preparing drilling and completion fluids having densities in the range of 11.5 to 19.2 lb/gal. The specific gravity of these fluids is also given.

Table 1

Zinc Bromide/Lithium Bromide Fluid
Density, Specific Gravity, and Weight Percent

Density at 70°F lb/gal	Sp.Gr.	$ZnBr_2$ wt.%	LiBr wt.%
13.5	1.62	2.2	52.4
13.8	1.66	7.0	49.0
14.1	1.69	11.5	45.7
14.4	1.73	14.5	43.6
14.7	1.77	20.2	39.5
15.0	1.80	24.1	36.7
15.3	1.84	28.0	34.0
15.6	1.87	31.7	31.2
15.9	1.91	35.2	28.8
16.2	1.95	38.7	26.3
16.5	1.98	42.0	23.9
16.8	2.02	45.2	21.6
17.1	2.05	48.2	19.4
17.4	2.09	51.2	17.3
17.7	2.13	54.0	15.3
18.0	2.16	54.8	14.7

Table 2

Zinc Bromide/Sodium Bromide Fluid

Density, Specific Gravity, and Weight Percent

Density at 70°F lb/gal	Sp.Gr.	$ZnBr_2$ wt.%	NaBr wt.%
13.0	1.56	6.3	43.0
13.5	1.62	12.1	40.2
14.0	1.68	17.6	37.6
14.5	1.74	22.6	35.2
15.0	1.80	27.3	33.0
15.5	1.86	31.7	30.9
16.0	1.92	35.9	28.9
16.5	1.98	39.7	27.1
17.0	2.04	43.4	25.3
17.5	2.10	46.8	23.7

TABLE 3

Zinc Bromide/Potassium Bromide Fluid

Density, Specific Gravity, and Weight Percent

Density at 70°F lb/gal	Sp.Gr.	$ZnBr_2$ wt.%	KBr wt.%
11.5	1.38	2.6	37.5
12.0	1.44	8.7	35.3
12.5	1.50	14.4	33.1
13.0	1.56	19.7	31.1
13.5	1.62	24.5	29.2
14.0	1.68	29.4	27.3
14.5	1.74	33.2	25.9
15.0	1.80	37.1	24.4
15.5	1.86	40.8	23.0
16.0	1.92	44.2	21.7
16.5	1.98	47.4	20.5
17.0	2.04	50.5	19.3
17.5	2.10	53.3	18.2
18.0	2.16	56.0	17.2

TABLE 4

Zinc Bromide/Sodium Bromide/Potassium Bromide Fluid

Density, Specific Gravity, and Weight Percent

Density at 70°F lb/gal	Sp.Gr.	$ZnBr_2$ wt.%	KBr wt.%	NaBr wt.%
13.0	1.56	7.1	2.2	40.0
13.5	1.62	13.6	4.2	34.7
14.0	1.68	19.7	6.0	29.7
14.5	1.74	25.3	7.8	25.1
15.0	1.80	30.6	9.4	20.8
15.5	1.86	35.5	10.9	16.8
16.0	1.92	40.1	12.3	13.0
16.5	1.98	44.4	13.6	9.5
17.0	2.04	48.5	14.9	6.1
17.5	2.10	52.4	16.1	3.0
18.0	2.16	56.0	17.2	0.0

Table 5

Zinc Bromide/Potassium Bromide Fluid
Density, Specific Gravity and Weight Percent

Density at 70°F lb/gal	Sp.Gr.	$ZnBr_2$ wt.%	KBr wt.%
11.5	1.38	3.0	37.0
12.0	1.44	10.0	33.5
12.5	1.50	16.5	30.3
13.0	1.56	22.5	27.3
13.5	1.62	28.0	24.3
14.0	1.68	33.1	21.9
14.5	1.74	37.9	19.5
15.0	1.80	42.3	17.3
15.5	1.86	42.5	20.0
16.0	1.92	42.7	22.5
16.5	1.98	42.9	24.9
17.0	2.04	43.1	27.1
17.5	2.10	43.3	29.3
18.0	2.16	43.4	31.2
18.5	2.22	43.6	33.1
19.0	2.28	43.7	34.9
19.2	2.31	43.8	35.6

Table 6

Zinc Bromide/Potassium Bromide Fluid

Density, Specific Gravity and Weight Percent

Density at 70°F lb/gal	Sp.Gr.	$ZnBr_2$ wt.%	KBr wt.%
13.0	1.56	7.7	41.4
13.5	1.62	14.9	37.1
14.0	1.68	21.5	33.2
14.5	1.74	27.7	29.5
15.0	1.80	33.5	26.0
15.5	1.86	35.1	27.3
16.0	1.92	36.5	28.5
16.5	1.98	37.9	29.6
17.0	2.04	39.2	30.7
17.5	2.10	40.4	31.7
18.0	2.16	41.5	32.6
18.5	2.22	42.6	33.5
19.0	2.28	43.6	34.4
19.2	2.31	44.0	34.7

All of the calcium-free fluids in the density range of 11.5 to 19.2 lb/gal described above may be prepared by mixing a two salt base fluid (e.g., 18.0 lb/gal $ZnBr_2$/KBr or 17.5 lb/gal $ZnBr_2$/NaBr) with single- or two-salt solutions having a lower density than the base fluid (e.g., 12.5 lb/gal NaBr or 15.0 lb/gal $ZnBr_2$/KBr). These fluids may also be formulated by mixing solutions of $ZnBr_2$ and LiBr, NaBr, or KBr and dry salts (e.g., 77 wt.% $ZnBr_2$, 54 wt.% LiBr, 46 wt.% NaBr, 38.5 wt.% KBr, and dry salts).

EXAMPLE II.

A NaBr solution having a density of 12.5 lb/gal was prepared by mixing 46.0 wt. % solid NaBr and 54.0 wt.% water. A $ZnBr_2$/NaBr base fluid having a density of 17.5 lb/gal was prepared by combining 46.8 wt. % solid $ZnBr_2$, 23.7 wt. % solid NaBr, and 29.5 wt. % water. Varying amounts of $ZnBr_2$/NaBr base fluid

(density, 17.5 lb/gal) were then mixed with different amounts of NaBr solution (density, 12.5 lb/gal) in order to prepare different completion fluids in the density range of 13.0 to 17.5 lb/gal. The volumes of the base fluid and NaBr solution required to formulate these different completion fluids, along with the respective densities and thermodynamic crystallization temperatures of the completion fluids, are given in Table 7.

TABLE 7

Blending Procedure-$ZnBr_2$/NaBr Fluid
Using 17.5 lb/gal $ZnBr_2$/NaBr and 12.5 lb/gal NaBr

Density at 70°F lb/gal	$ZnBr_2$/NaBr bbl	NaBr bbl	Cryst.Pt. (TCP) °F
12.5	0.000	1.000	21
13.0	0.100	0.900	18
13.5	0.200	0.800	15
14.0	0.300	0.700	10
14.5	0.400	0.600	1
15.0	0.500	0.500	-16
15.5	0.600	0.400	-3
16.0	0.700	0.300	9
16.5	0.800	0.200	23
17.0	0.900	0.100	37
17.5	1.000	0.000	47

The low pH and relatively low concentrations of the divalent salt in these fluids (compared with $ZnBr_2/CaBr_2/CaCl_2$ fluids) make them particularly suitable for use in formations with high carbonate and/or high sulfate concentrations.

EXAMPLE III.

Another calcium-free completion fluid was prepared by mixing a $ZnBr_2$/LiBr base fluid with a LiBr solution. The 18.0 lb/gal $ZnBr_2$/LiBr base fluid was prepared by combining an appropriate volume of aqueous 77 wt % $ZnBr_2$ solution (density, 20.3

lb/gal) with the requisite amount of aqueous 54 wt % LiBr solution (density, 13.4 lb/gal). Different $ZnBr_2$/LiBr fluids with densities in the range of 14.0 to 18.0 lb/gal were then formulated by combining varying amounts of the 18.0 lb/gal $ZnBr_2$/LiBr base fluid with different volumes of the aqueous 13.4 lb/gal LiBr solution. Table 8 provides the different volumes of base fluid and LiBr solution required to formulate these completion fluids and the thermodynamic crystallization temperatures of the fluids.

Table 8

Mixing Procedure-$ZnBr_2$/LiBr Fluid
Using 18.0 lb/gal $ZnBr_2$/LiBr and 13.4 lb/gal LiBr

	Composition for 1 bbl (42 gal)		
Density of 70°F lb/gal	$ZnBr_2$/LiBr bbl	LiBr bbl	Cryst.Pt. (TCP)°F
13.5	0.030	0.960	-60°F
13.8	0.097	0.893	
14.1	0.164	0.826	
14.4	0.209	0.781	
14.7	0.298	0.687	
15.0	0.362	0.618	
15.3	0.428	0.552	
15.6	0.496	0.484	
15.9	0.557	0.418	
16.2	0.625	0.350	
16.5	0.691	0.284	
16.8	0.759	0.216	
17.1	0.820	0.150	
17.4	0.890	0.085	
17.7	0.956	0.019	
18.0	1.000	0.000	

EXAMPLE IV.

A different calcium free completion fluid, $ZnBr_2/KBr$, was prepared in two ways. The 18.0 lb/gal base fluid was prepared by combining the appropriate amount of the aqueous 77 wt % $ZnBr_2$ solution with the requisite volume of the aqueous 38.5 wt % KBr solution (density, 11.3 lb/gal). This method of preparation was not preferred however because of the low density (i.e., 11.3 lb/gal) of the aqueous 38.5 wt % KBr solution. Mixing of the low density KBr solution with the $ZnBr_2$ solution resulted in a base fluid with an inordinately high $ZnBr_2$ concentration. The preferred method was to dilute the aqueous 77 wt % $ZnBr_2$ with water and then add the required weight of solid KBr to achieve a 18.0 lb/gal base fluid. This base fluid can then be mixed with the 11.3 lb/gal aqueous KBr solution to prepare different completion fluids having densities in the range of 11.5 to 18.0 lb/gal. Table 9 presents the various mixtures of base fluids and KBr solutions used to make the completion fluids of Example IV along with the thermodynamic crystallization temperatures for these completion fluids.

TABLE 9

Blending Procedure - $ZnBr_2$/KBr Fluid
Using 18.0 lb/gal $ZnBr_2$/KBr and 11.3 lb/gal KBr
Composition for 1 bbl (42 gal)

Density at 70°F lb/gal	$ZnBr_2$/KBr bbl	KBr bbl	Cryst.Pt. (TCP) °F
12.0	0.104	0.896	6
12.5	0.179	0.821	
13.0	0.254	0.746	-8
13.5	0.328	0.672	
14.0	0.403	0.579	-12
14.5	0.478	0.522	
15.0	0.552	0.448	
15.5	0.627	0.373	-35
16.0	0.701	0.299	
16.5	0.776	0.224	-64
17.0	0.851	0.149	
17.5	0.925	0.075	-23
18.0	1.000	0.000	

Because of their low crystallization temperatures (6 to -64°F), these completion fluids can be used during the winter months without danger of solidification.

EXAMPLE V.

Another calcium-free fluid may be prepared by dissolving $ZnBr_2$, NaBr, and KBr salts in water. As an example of the numerous ways of preparing completion fluids, a 18.0 lb/gal $ZnBr_2$/KBr base fluid (prepared according to Example IV) was mixed with a an aqueous solution of NaBr having a density 12.5 lb/gal to formulate $ZnBr_2$/NaBr/KBr fluids having densities in the range of 13.0 to 18.0 lb/gal. The various volumes of the base fluid and NaBr solution used in these completion fluids are given in Table 10.

TABLE 10

Blending Procedure-$ZnBr_2$/KBr/NaBr Fluid
Using 18.0 lb/gal $ZnBr_2$/KBr and 12.5 lb/gal NaBr
Composition for 1 bbl (42 gal)

Density at 70°F lb/gal	$ZnBr_2$/KBr bbl	NaBr bbl
13.0	0.091	0.909
13.5	0.182	0.818
14.0	0.273	0.727
14.5	0.364	0.636
15.0	0.455	0.545
15.5	0.546	0.454
16.0	0.636	0.364
16.5	0.727	0.273
17.0	0.818	0.182
17.5	0.909	0.091
18.0	1.000	0.000

EXAMPLE VI.

Calcium-free completion fluids having densities greater than 18.0 lb/gal. may be prepared by dissolving a greater amount of solid monovalent salt (i.e., NaBr, KBr, or LiBr) into the base fluids than in the previous examples. For example, a 20.5 lb/gal. $ZnBr_2$/NaBr completion fluid was prepared by dissolving solid NaBr in a 17.5 lb/gal. $ZnBr_2$/NaBr base fluid. It has also been discovered that 19.2 lb/gal. calcium-free base fluids having low composition of $ZnBr_2$ (42-44 wt.%) by dissolving solid monovalent salt into the zinc bromide solution. Owing to the high composition of monovalent salt in these base fluids, if they are blended down with lower density base fluids (i.e. 11.3 lb/gal. KBr, 12.5 lb/gal. NaBr, or 13.4 lb/gal. LiBr), solid monovalent salt will precipitate out of the solution (salting out). The problem was resolved by formulating an intermediate density base fluid (15.0 lb/gal.) by blending the 77 wt.% $ZnBr_2$ solution with the lower density base fluids. These new base fluids were then used with

19.2 lb/gal. fluids to blend up and with lower density base fluids to blend down.

The composition of $ZnBr_2$ in the new 19.2 lb/gal. base fluids is about 42.0 - 44.0 wt.%. Because of lower concentrations of $ZnBr_2$/KBr in these base fluids compared with those used in Examples I-V, they are less corrosive to metal equipment than the base fluids used in the previous examples.

EXAMPLE VII

A 19.2 lb/gal $ZnBr_2$/KBr base fluid was prepared by adding 7.1g water to 56.9g 77 wt.% $ZnBr_2$ and then dissolving 36.0 solid 99 wt.% KBr into the resulting solution. The composition of this fluid is therefore 43.8 wt.% $ZnBr_2$/KBr, 35.6 wt.% KBr and 20.6 wt.% water.

A 15.0 lb/gal $ZnBr_2$/KBr base fluid was prepared by mixing 140.7 ml of 77 wt.% $ZnBr_2$ solution (d = 20.3 lb/gal) with 209.8 ml of 38.5 wt.% KBr solution (d = 11.3 lb/gal). The resulting fluid contained 42.3 wt.% $ZnBr_2$, 17.3 wt.% KBr and 40.4 wt.% water.

Tables 11 and 12 present the blending procedures for $ZnBr_2$/KBr fluids using 19.2 lb/gal $ZnBr_2$/KBr, 15.0 lb/gal $ZnBr_2$/KBr and 11.3 lb/gal KBr. The thermodynamic crystallization temperatures are also given in Tables 11 and 12.

Table 11

Blending Procedure for $ZnBr_2$/KBr Fluid
Using 15.0 lb/gal $ZnBr_2$/KBr and 11.3 lb/gal KBr

Density at 70°F lb/gal	15.0 lb/gal $ZnBr_2$/KBr bbl	11.3 lb/gal KBr bbl	Cryst.Pt. (TCP) °F
11.5	0.054	0.946	
12.0	0.189	0.811	6.8
12.5	0.324	0.676	
13.0	0.460	0.540	- 0.4
13.5	0.595	0.405	
14.0	0.730	0.270	-11.6
14.5	0.865	0.135	
15.0	1.000	0.000	-36.0

Table 12

Blending Procedure for $ZnBr_2$/KBr Fluid
Using 19.2 lb/gal and 15.0 lb/gal $ZnBr_2$/KBr

Density at 70°F lb/gal	19.2 lb/gal bbl	15.0 lb/gal bbl	Cryst.Pt. (TCP) °F
15.5	0.119	0.881	
16.0	0.238	0.762	-27.9
16.5	0.357	0.643	
17.0	0.476	0.524	-24.5
17.5	0.595	0.405	
18.0	0.714	0.286	-12.6
18.5	0.833	0.167	
19.0	0.952	0.048	
19.2	1.000	0.000	3.0

Example VIII

A 19.2 lb/gal $ZnBr_2$/NaBr base fluid was prepared by adding 8.2g water to 57.1g 77 wt.% $ZnBr_2$ solution and then dissolving 34.7g 97 wt.% dry NaBr into the resulting solution. The composition of this fluid was therefore 44.0 wt.% $ZnBr_2$, 34.7 wt.% NaBr and 21.3 wt.% water. Another zinc bromide/sodium bromide base fluid (15.0

lb/gal) was prepared by mixing 112.4 ml of 77 wt.% $ZnBr_2$ solution (d = 20.3 lb/gal) with 237.6 ml of 46.0 wt.% NaBr solution (d = 12.5 lb/gal). The resulting fluid contained 33.5 wt.% $ZnBr_2$, 26.0 wt.% NaBr and 40.5 wt.% water.

Tables 13 and 14 present the blending procedures for $ZnBr_2$/NaBr fluids using 19.2 lb/gal and 15.0 lb/gal $ZnBr_2$/NaBr, and 12.5 lb/gal NaBr. The thermodynamic crystallization temperatures for these fluids are also given in Tables 13 and 14.

Table 13

Blending Procedure for $ZnBr_2$/NaBr Fluid
Using 15.0 lb/gal $ZnBr_2$/NaBr and 12.5 lb/gal NaBr

Density at 70°F lb/gal	15.0 lb/gal $ZnBr_2$/NaBr bbl	12.5 lb/gal NaBr bbl	Cryst.Pt. (TCP) °F
13.0	0.200	0.800	5.6
13.5	0.400	0.600	
14.0	0.600	0.400	-35.3
14.5	0.800	0.200	
15.0	1.000	0.000	-27.7

Table 14

Blending Procedure for $ZnBr_2$/NaBr Fluid Using 19.2 lb/gal and 15.0 lb/gal $ZnBr_2$/NaBr

Density at 70°F lb/gal	19.2 lb/gal bbl	15.0 lb/gal bbl	Cryst.Pt. (TCP) °F
15.5	0.119	0.881	
16.0	0.238	0.762	2.8
16.5	0.357	0.643	
17.0	0.476	0.524	24.4
17.5	0.595	0.405	
18.0	0.714	0.286	39.7
18.5	0.833	0.167	
19.0	0.952	0.048	
19.2	1.000	0.000	48.6

FORMATION DAMAGE EXPERIMENTS

Formation damage experiments have shown that, when 18.0 lb/gal $ZnBr_2$/KBr or 17.5 lb/gal $ZnBr_2$/NaBr completion fluids were mixed with a 2/8 ratio of formation brine having a high carbonate and/or high sulfate concentration, no precipitate was formed. However, when the same experiments were performed with a 18.0 lb/gal $ZnBr_2/CaBr_2$ completion fluid, a white precipitate was formed. In other experiments, 14.5 lb/gal $ZnBr_2$/NaBr and $ZnBr_2$/KBr completion fluids were mixed separately with a 3/7 ratio of formation brine and no precipitate was formed. However, when the same test was performed with a 14.5 lb/gal $ZnBr_2/CaBr_2$ completion fluid, a white precipitate was formed.

Considering the solubility products for calcium carbonate (i.e., 3.8×10^{-9} at 25 °C) and zinc carbonate (i.e., 2.1×10^{-11} at 25°C), it would be expected that zinc carbonate and calcium carbonate would precipitate when $ZnBr_2$/NaBr or $ZnBr_2$/KBr completion fluids were mixed with formation brine. However, no precipitates formed with the solutions of this invention. The novelty of the present invention lies in the discovery that the

substitution of either sodium bromide or potassium bromide for calcium bromide alters the expected reaction between zinc and carbonate ions such that no insoluble zinc carbonate precipitate is formed. Without being limited to the correctness of any particular theory this unusual effect may be due to a lower pH and a lower concentration of divalent metal ions in the calcium-free completion fluids than in the standard $ZnBr_2/CaBr_2$ completion fluids. Another possible explanation is that zinc bromide, sodium bromide, potassium bromide and lithium bromide may form double salts in aqueous solution, preventing zinc carbonate precipitation. Still another possible explanation is the formation of complex ions between zinc ions and bromide ions, i.e., $ZnBr^+$, $ZnBr_3^-$, $ZnBr_4^=$ which may prevent the carbonate precipitation. Also, the reported solubility products for $CaCO_3$ and $ZnCO_3$ are those at infinite dilution or when the activity coefficient of the ions involved approach unity. In the concentrated salt solutions of the present invention, the activity coefficients of calcium, zinc and carbonate ions may, due to high ionic strength, be different than unity, and hence the reported values for solubility products of $ZnCO_3$ and $CaCO_3$ cannot be used as a criteria for predicting the formation of precipitates. Whatever the explanation, it is clear that, most unexpectedly, the calcium-free fluids of this invention may quite successfully be employed with carbonate and sulfate containing formation brines without precipitation of insoluble zinc salts.

VISCOSIFICATION EXPERIMENTS

The calcium-free completion fluids of the present invention can be easily viscosified with any HEC-based liquid viscosifier. Tables 15 and 16 presents the funnel viscosities and rheology data for different $ZnBr_2/NaBr$ and $ZnBr_2/KBr$ fluids viscosified with HEC-based liquid viscosifier.

Table 15

Funnel Viscosity and Rheology Data
for Calcium-Free Fluids ($ZnBr_2$/NaBr)
Viscosified With 15 lb/bbl HEC-Based Liquid Viscosifier
---One Hour Mixing---

Fluid Density at 70°F lb/gal	Funnel Viscosity (sec)	Fann RPM 600	Fann RPM 300	Apparent Viscosity cp	Plastic Viscosity cp	Yield Point lb/100 sqft
15.0	366	269	213	135	86	157
15.5	419	285	230	143	55	175
16.0	409	OS	241	OS	OS	OS
16.5	383	OS	240	OS	OS	OS
17.5	595	OS	279	OS	OS	OS
19.0	1195	OS	OS	OS	OS	OS

OS = off scale, greater than 300

Table 16

Funnel Viscosity and Rheology Date for Calcium-Free
Fluids ($ZnBr_2$KBr) Viscosified with 15 lb/bbl
HEC-Based Liquid Viscosifier

Fluid Density at 70°F lb/gal	Funnel Viscosity (sec)	Fann RPM 600	Fann RPM 300	Apparent Viscosity cp	Plastic Viscosity cp	Yield Point lb/100 sqft
15.0	210	226	183	113	43	140
15.5	310	260	214	130	46	168
16.0	350	259	207	130	52	155
16.5	320	276	224	138	52	172
17.5	605	OS	289	OS	OS	OS
18.5	530	OS	286	OS	OS	OS
19.0	471	OS	281	OS	OS	OS

OS = off-scale, greater than 300

These data show that the 15 lb/bbl HEC-based liquid viscosifier was effective as a viscosifier for zinc ion-containing fluids in the density range of 15.5 to 19.0 lb/gal. The funnel viscosity

measurements, which cannot be manipulated mathematically, are presented with the measurements obtained from the viscometer for purposes of permitting comparison of these completion fluids fluid viscosities. A viscosified fluid used as a "pill" should exhibit a funnel viscosity of about 200 sec. The data in Tables 15 and 16 indicate that concentrations of 10 to 15 lb/bbl of the HEC-based liquid viscosifier are sufficient to generated funnel viscosities of 200 sec.

TOXICITY EXPERIMENTS

Toxicity data for the calcium-free fluids of the present invention indicates that these fluids may be safely employed. While zinc bromide solution has been found to be a primary eye irritant, neither zinc bromide nor any of the mon-ovalent salt solutions (LiBr, NaBr, and KBr) has been considered primary skin irritants. Table 10 contains LD_{50} (i.e., the lethal dosage at which 50% of the test animals die) toxicity data from the 1981-82 Registry of Toxic Effects of Chemical Substances from the United States Department of Health, Education and Welfare. See also Sax, Dangerous Properties of Industrial Materials, 6th ed., or the Merck Index, 10th ed.

CORROSION INHIBITION

Seven day corrosion rates were determined in a manner known to those skilled in the art for calcium-free completion fluids in accordance with this invention using thioglycolate/ thiocyanate-based corrosion inhibitors. Specific corrosion inhibitors tested included a mixture of sodium thiocyante, ammonium thioglycolate and sodium isoascorbate ("C.I.A."); calcium thiocyanate ("C.I.B."); and sodium thiocyanate ("C.I.C.").

Table 17

Seven Day Corrosion Rates of Mild Steel
Coupons in Calcium-Free Fluids

Fluid Density at 70°F. (lb/gal)	Temp. (°F)	Inhibitor	Corrosion Rate (mpy)
18.0[a] $ZnBr_2$/KBR	300	Blank	610
18.0 $ZnBr^2$/KBR	300	C.I.A.	15
18.0 $ZnBr_2$/KBR	300	C.I.B.	20
17.0[b] $ZnBr_2$/KBr	350	Blank	350
17.0 $ZnBr_2$/KBr	350	C.I.A.	7
17.5[c] $ZnBr_2$/NaBr	300	Blank	456
17.5 $ZnBr_2$/NaBr	300	C.I.A.	14
17.5 $ZnBr_2$/NaBr	300	C.I.B.	19
14.5 $ZnBr_2$/NaBr	300	Blank	52
14.5 $ZnBr_2$/NaBr	300	C.I.A.	8
19.0[d] $ZnBr_2$/KBr	350	Blank	112
19.0 $ZnBr_2$/KBr	350	C.I.A.	9
19.0 $ZnBr_2$/KBr	350	C.I.B.	8
19.0 $ZnBr_2$/KBr	350	C.I.C.	8
19.0[e] $ZnBr_2$/NaBr	350	Blank	53
19.0 $ZnBr_2$/NaBr	350	C.I.A.	6
19.0 $ZnBr_2$/NaBr	350	C.I.B.	7
19.0 $ZnBr_2$/NaBr	350	C.I.C.	9

a 56.2 wt.% $ZnBr_2$/17.3 wt.% KBr
b 50.3 wt.% $ZnBr_2$/19.4 wt.% KBr
c 52.0 wt.% $ZnBr_2$/18.0 wt.% NaBr
d 43.2 wt.% $ZnBr_2$/35.6 wt.% KBr
e 42.5 wt.% $ZnBr_2$/34.5 wt.% NaBr

These data show that thioglycolate and thiocyanate group containing corrosion inhibitors act as effective corrosion inhibitors for zinc containing solutions of the present invention.

CLAIMS

1. A clear, high-density calcium-free fluid adapted for use as well completion, packing and perforating media comprising an aqueous solution of zinc bromide and at least one member selected from the group consisting of lithium bromide, sodium bromide, and potassium bromide, the solution having a density lying in the range of about 11.5 to 20.5 pounds per gallon and a pH lying in the range of about 1.0 to 7.5.

2. A clear, calcium-free fluid in the density range adapted for use as well completion, packing and perforating media comprising an aqueous solution of zinc bromide and sodium bromide having a density of about 12.5 to about 19.2 pounds per gallon.

3. A clear, calcium-free fluid in the density range adapted for use as well completion, packing and perforating media comprising an aqueous solution of zinc bromide and lithium bromide having a density of about 13.5 to about 18.0 pounds per gallon.

4. A clear calcium-free fluid in the density range adapted for use as well completion, packing and perforating media comprising an aqueous solution of zinc bromide and potassium bromide having a density of about 12 to about 19.2 pounds per gallon.

5. A clear calcium-free fluid in the density range adapted for use as well completion, packing and perforating media comprising an aqueous solution of zinc bromide, potassium bromide, and sodium bromide having a density of about 13.0 to about 18.0 pounds per gallon.

6. A clear, high density calcium-free fluid, as claimed in Claim 1, and further comprising an effective amount of thioglycolate and/or thiocyanate group containing corrosion inhibitor.

7. A clear, high density calcium-free fluid, as claimed in Claim 1, and further comprising an effective amount of an hydroxyethyl cellulose based viscosfying agent.

8. A method for drilling, completion or workover of wells comprising injecting into the well a clear, high-density calcium-free fluid, as claimed in Claim 1.

AMENDED CLAIMS

[received by the International Bureau on 23 December 1987 (23.12.87); original claims 1-5 amended; new claim 9 added (2 pages)]

1. (Amended) A clear, high-density calcium-free fluid adapted for use as well completion, packing and perforating media comprising an aqueous solution of about 2 up to about 55 percent by weight zinc bromide and about 15 up to about 54 percent by weight of at least one member selected from the group consisting of lithium bromide, sodium bromide, and potassium bromide, the solution having a density lying in the range of about 11.5 to 20.5 pounds per gallon and a pH lying in the range of about 1.0 to 7.5.

2. (Amended) A clear, calcium-free fluid in the density range adapted for use as well completion, packing and perforating media comprising an aqueous solution of about 6 up to about 47 percent by weight zinc bromide and about 24 up to about 43 percent by weight sodium bromide, the solution having a density of about 12.5 to about 19.2 pounds per gallon.

3. (Amended) A clear, calcium-free fluid in the density range adapted for use as well completion, packing and perforating media comprising an aqueous solution of about 2 up to about 55 percent by weight zinc bromide and about 15 up to about 54 percent by weight lithium bromide, the solution having a density of about 13.5 to about 18.0 pounds per gallon.

4. (Amended) A clear, calcium-free fluid in the density range adapted for use as well completion, packing and perforating media comprising an aqueous solution of about 3 up to about 56 percent by weight zinc bromide and about 17 up to about 38 percent by weight potassium bromide, the solution having a density of about 12 to about 19.2 pounds per gallon.

5. (Amended) A clear, calcium-free fluid in the density range adapted for use as well completion, packing and perforating media comprising an aqueous solution of about 7 up to about 56 percent by weight zinc bromide, about 2 up to about 17 percent by weight potassium bromide, and greater than 0 up to about 40 percent by weight sodium bromide, the solution having a density of about 13.0 to about 18.0 pounds per gallon.

6. A clear, high density calcium-free fluid, as claimed in Claim 1, and further comprising an effective amount of thioglycolate and/or thiocyanate group containing corrosion inhibitor.

7. A clear, high density calcium-free fluid, as claimed in Claim 1, and further comprising an effective amount of an hydroxyethyl cellulose based viscosfying agent.

8. A method for drilling, completion or workover of wells comprising injecting into the well a clear, high-density calcium-free fluid, as claimed in Claim 1.

9. A clear, calcium-free fluid, as claimed in any of claims 1 to 5, wherein the solution comprises not more than about 44 percent zinc bromide by weight.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/01796

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

E21B43/00 IPC-4

252/8.551 U.S.

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	252/8.551, 8.51, 8.514, 8.555

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
P,X	US, A, 4,619,773, HEILWEIL et al., 28 October 1986	1-8
X	US, A, 4,554,081, BORCHARDT et al., 19 November 1985	1-8
P,X	US, A, 4,609,476, HEILWEIL, 02 September 1986	1-8
P,X	US, A, 4,615,740, PELEZO et al., 07 October 1986	1-8
Y	GB, A, 2,027,686, COFFEY, 27 February 1980 (Note page 1, lines 31-55 and page 5, lines 22-32 and lines 44-54)	6
Y	GB, A, 2,121,397, HANDY, 21 December 1983 (Note page 2 lines 28-47)	6
A	US, A, 4,292,183, SANDERS, 29 September 1981	1-8
A	US, A, 4,415,463, MOSIER et al., 15 November 1983	1-8
A	US, A, 4,420,406, HOUSE et al., 13 December 1983	1-8

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
16 October 1987	30 OCT 1987
International Searching Authority [1]	**Signature of Authorized Officer** [20]
ISA/US	Herbert B. Guynn